Final: 12/22/98

**DMMP CLARIFICATION PAPER**
**SMS TECHNICAL INFORMATION MEMORANDUM**

# TRIBUTYLTIN ANALYSIS: CLARIFICATION OF INTERSTITIAL WATER EXTRACTION AND ANALYSIS METHODS - INTERIM

Prepared by Erika Hoffman (U.S. EPA, 206-553-0038) for the DMMP agencies.

## INTRODUCTION

Tributyltin (TBT)[1] is a special chemical of concern under the Dredged Material Management Program (DMMP). Testing for this chemical in areas where it is likely to be found (e.g. marinas, ship repair facilities, navigation channels) may be required under this program. The available literature indicates that the toxicity and bioaccumulation of TBT are affected by a variety of factors, including organic carbon in sediment and water, pH, salinity, clay fraction, and the presence of constituents such as iron oxides. In addition, TBT exists in several forms, is released into the aquatic environment in different ways, and the mode of exposure to benthic organisms varies.

In 1996 the DMMP/SMS agencies reviewed the available literature and concluded that analysis of bulk sediment TBT was not the most environmentally relevant way to assess the bioavailability of TBT (EPA, 1996, Michelsen *et al*., 1996). Due to the way in which TBT acts and reacts in the environment, the agencies determined that analysis of interstitial water for the presence of TBT was a more effective way to measure its potential for impact in the aquatic environment. As a part of the Sediment Management Annual Review process, the agencies adopted the requirement for interstitial water analysis in 1996.

## PROBLEM IDENTIFICATION

A number of questions have been raised regarding sampling and analysis for TBT since the agencies initiated the requirement for interstitial water testing. Many different approaches are used for the extraction and preparation of interstitial water from sediment samples and it is generally believed that both technique and materials can cause large variations in the measured interstitial water TBT concentration. In particular, there are concerns that certain steps in the extraction and preparation process may contribute to the loss of TBT in the pore-water. Some of the most important unresolved issues involving the measurement of TBT in interstitial water include:

- The degree of TBT adsorption to various laboratory materials (such as stainless steel, and borosilicate glass) and equipment (such as centrifuge tubes, filters and filtration apparatus).

[1] Although this clarification paper focuses on tributyltin, the procedures and guidance presented herein apply to the measurement of all organotin species (e.g., mono-, di-, tri-, and tetrabutyltin).

- The effect of aerobic conditions on TBT solubility.
- The effect of sediment and interstitial water extract holding time on TBT solubility.
- Differing partitioning characteristics of TBT in fresh water versus marine environments.
- The relative toxicological importance if colloid-bound TBT versus soluble TBT in porewater.

Avocet Consulting and Striplin Environmental Associates (SEA) investigating these and other unresolved issues surrounding butyl tin extraction, analysis, and data use. The study is divided into two phases. The first phase includes distribution of a policy and comprehensive analytical questionnaire (November, 1998), a follow-up regulatory workshop (January, 1999), and finalization of the analytical work plan based on questionnaire and workshop responses. The second phase consists of analysis of actual environmental samples, data validation, data interpretation and write-up, and preparation of a SMARM clarification paper. The ultimate goal of the Avocet/SEA study and of this clarification paper is to further the development of a DMMP standard protocol for extracting and measuring TBT in sediment interstitial water.

**The following clarifications are provided as *interim* guidance to ensure that all projects reporting TBT data utilize similar methods for interstitial water extraction and TBT analysis. The agencies recognize that project-specific constraints may require deviations from the methods and performance criteria described below. Any such deviation must be justified and approved by the DMMP agencies prior to test initiation.**

**PROPOSED CLARIFICATIONS FOR THE TBT-INTERSTITIAL WATER PROTOCOL**

The following proposed ***interim*** guidance should be applied to all DMMP projects for which interstitial water TBT analysis is required. This guidance was developed based on input from researchers and technical staff who regularly extract and measure interstitial water TBT. It reflects current thought on the best methodology for limiting the loss of TBT due to sample handling. The DMMP agencies are aware that new methodologies to refine TBT analysis may be in development and will consider updating these interim guidelines with any alternative methods that may yield equal or better results. This interim guidance will be revisited at a later date by the DMMP agencies once the results of the Avocet/SEA study (described above) as well as results from other project-specific testing are available.

## 1. Materials

***Field collection and storage*** - Polycarbonate, borosilicate glass or stainless steel containers should be used for field collection, homogenization, and pre-centrifugation storage of sediments to be tested for interstitial water TBT.

***Centrifugation and interstitial water collection***– Polycarbonate containers should be used for centrifugation and for supernatant collection after the first round of spinning since use of polycarbonate minimizes loss of TBT due to sorption. Borosilicate glass storage containers may be used to store the acidified supernatant collected after the second round of centrifugation.

***Interstitial water analysis*** – Borosilicate glass or polycarbonate equipment and containers may be used when handling and extracting acidified interstitial water samples.

## 2. Equipment Decontamination and Cleaning

All laboratory equipment and glassware used for sediment collection and storage, interstitial water collection and storage, and TBT analysis should be appropriately cleaned and rinsed with residue analysis grade solvents. The effectiveness of any given decontamination procedure will ultimately be demonstrated by meeting the appropriate QC performance criteria (see Table 1). The following are examples of acceptable procedures for the cleaning and decontamination of polycarbonate and other material:

| Polycarbonate | All other materials |
|---|---|
| Detergent wash | Detergent wash |
| Rinse with dilute hydrochloric acid | Rinse with deionized water |
| Rinse with deionized water | Rinse with acetone |
| Rinse with 0.1% tropolone/hexane | Rinse with 0.1% tropolene/$MeCl_2$ |
| Rinse with hexane | Rinse with methylene chloride |

3. **Sediment Sampling and Holding**

When loading sediment samples into storage containers, headspace should be minimized and containers purged with nitrogen either in the field or upon arrival at the laboratory (before storage). Because the freezing of bulk sediment samples may result in structural changes in the sediment which will alter the availability of TBT, samples to be held for future TBT analysis should have interstitial water extracted prior to freezing. Sediment samples should be maintained in the dark at 4°C while in transport and once in the laboratory. It is important to minimize sample holding time prior to centrifugation in order to reduce the chance for adsorptive loss of TBT. No more than 7 days should elapse between sediment collection and centrifugation.

4. **Interstitial Water Collection Method**

Centrifugation is preferred for collecting sediment interstitial water following the procedure in paragraph 5 (below). Alternative interstitial water extraction methods may be used in cases where centrifugation is not an effective technique, (e.g., for very sandy sediments) and will be decided on a case-by-case basis by the DMMP agencies.

**5. Centrifugation Procedure**

***Sample preparation*** - Pooled interstitial water that may collect on the surface of the sediment sample while in storage should be reintroduced into the sample prior to centrifugation. Samples should be maintained at or below 11 °C during processing.

***Anaerobic extraction*** - Sample loading, supernatant/interstitial water decanting, transfer, and sample acidification should occur under anaerobic conditions (i.e., under a nitrogen atmosphere).

***Centrifuge settings*** - Samples should be double centrifuged with the first run at 3000 G for 30 minutes and the second run within the range of 3000 – 9000 G for 30 minutes. Samples should be maintained at a temperature at or below 11°C during centrifugation. Extra care should be taken to minimize carryover when transferring supernatant after each centrifugation step. A new and potentially useful method for obtaining particle-free interstitial water using an aspiration system is described in Ozretich and Schults (1998).

## 6. Filtration

Filtration should not be performed on interstitial water samples. The DMMP agencies will reconsider the question of whether or not to filter interstitial water pending results of the Avocet/SEA study (described above) and any other studies addressing the influence of filters and the filtration process on TBT sorption.

## 7. Interstitial Water Handling

Interstitial water should be acidified with hydrochloric acid immediately after centrifugation and stored in pre-cleaned containers (borosilicate glass or polycarbonate) at 4°C. No more than 7 days should elapse between interstitial water collection and the initiation of TBT analysis.

## 8. Analytical Methods

Acceptable methods for measuring TBT involve tropolone/methylene chloride extraction, followed by Grignard derivitization and analysis by GC/MS (e.g., Krone *et al*., 1989), GC/MS SIM (e.g., PSEP, 1997), or GC/FPD (e.g., Unger *et al*., 1986).

## 9. Performance Criteria for Sample Collection and Interstitial Water TBT Analysis

The DMMP agencies have decided to recommend QC performance criteria rather than providing a step-by-step protocol for the extraction, derivitization, and analysis of TBT. The criteria presented in Table 1 must be met in order to verify that cleaning, extraction and derivitization methods are being performed correctly. Laboratories will be required to meet these performance criteria as well as take the specified corrective action if performance criteria are not met. Deviations from the specified performance criteria will be considered by the DMMP agencies on a project-specific basis. Justification for alternative performance criteria must be submitted in writing and receive agency approval prior to the initiation of testing. As discussed in earlier guidance (Michelsen, *et al*., 1996), TBT analytical results and QC information should be reported as the TBT ion.

Table 1. Summary of Quality Control Procedures for TBT in Interstitial water

| QC Check | Minimum Frequency | Acceptance Criteria | Corrective Action |
|---|---|---|---|
| Laboratory Control Sample (LCS) * | 1 per analytical batch (≤ 20 samples) | Recovery 50 – 150% | 1. Check calculations<br>2. Reanalyze (matrix or injection problems?)<br>3. If still out, re-extract and reanalyze LCS and assoc. samples (if available); If not available flag data. |
| Matrix spike (MS) and matrix spike duplicate (MSD) * | 1 MS/MSD pair per analytical batch (≤ 20 samples) | Recovery 50 – 150% and relative percent difference (RPD) ≤ 30% | 4. Evaluate for supportable matrix effect.<br>5. If no interference, re-extract and reanalyze MS/MSD once (if available).<br>6. If still out, report both sets of data. |
| Surrogate spike * (Tripentyltin recommended) | 1 per sample | Recovery 50 – 150% | 7. Check calculations.<br>8. Evaluate for supportable matrix effect<br>9. If no interference is evident, re-extract and reanalyze affected sample(s) (if available) and flag any outliers. |
| Method blank** | 1 per analytical batch (≤ 20 samples) | Target analyte < 3x the reporting limit (RL) | 10. Flag if target > 3x RL but less than 0.075 ppb***.<br>11. Rerun batch and ID contamination source if target >0.075 ppb. |

* All QC samples should be run using the same sample handling as is used on the environmental samples.
** Method blank can include centrifugation step or, alternatively a centrifugation blank can be run separately from the analytical method blank.
*** 0.075 ppb TBT is used here as a benchmark for evaluating blank performance because it represents a concentration that is one-half the interstitial water screening level (0.15 ppb) that is being used by the DMMP agencies to determine the need for bioaccumulation testing. Note that a minimum interstitial water volume of 200-500 ml will be needed to attain reporting limits less than 0.075 ppb TBT.

## REFERENCES

EPA. 1996. Recommendations for Screening Values for Tributyltin in Sediments at Superfund Sites in Puget Sound, WA. Prepared for EPA Region 10, Superfund by Roy F. Weston, Seattle, WA.

Krone, C.A., D.W. Brown, D.G. Burrows, S.L. Chan, and U. Varanasi. 1989. A method for analysis of butyltin species in measurement of butyltins in sediment and English sole livers from Puget Sound. Marine Environmental Research 27:1-18.

Michelsen, T., T.C. Shaw, and S. Stirling. 1996. Testing, reporting and evaluation of tributyltin data in PSDDA and SMS programs. Final PSDDA Issue Paper/SMS Technical Information Memorandum, October 1996.

Ozretich, R.J., and D.W. Schults. 1998. A comparison of interstitial water isolation methods demonstrates centrifugation with aspiration yields reduced loses of organic constituents. Chemosphere, Vol. 36, No. 3, pp. 603-615.

PSEP. 1997. Recommended guidelines for measuring organic compounds in Puget Sound water, sediment and tissue samples. Appendix B, Guidance for selected ion monitoring. Puget Sound Estuary Program. Prepared for U.S. Environmental Protection Agency Region 10, Seattle, WA.

Unger, M.A., W.G. McIntyre, K. Greaves, and R.J. Huggett, 1986. GC Determination of butyltins in natural waters by flame photometric detection of hexyl derivatives with mass spectrometric confirmation. Chemosphere 15:461.